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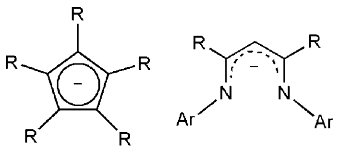
Nacnac … Are You Still There? The Evolution of β-Diketiminate Complexes of Nickel

*Daniel J. Mindiola**

β-diketiminate ligands · dinitrogen · iron · nickel · reduction

Much like the ubiquitous cyclopentadienyl ligand (Scheme 1, $R = CH_3$ or alternating positions for bulkier groups), the β-diketiminate class, generally denoted as "nacnac", or $\{ArNC(R)\}_2CH^-$ (where Ar = aryl and $R = CH_3$ or bulkier group, Scheme 1), occupies a rightful place alongside a narrow list of popular ancillary supports, given its ability to stabilize or generate unique coordination environments and to support reactive organometallic reagents or catalysts.[1] The nacnac ligand skeleton is analogous to the acac (acetylacetonate) ligand, but the oxygen atoms are exchanged for nitrogen-based moieties such as NR (R = alkyl, silyl, Ar). As a result, the substituent at the nitrogen donor atom can allow for steric protection at the metal center unlike acac could offer. The explosion in popularity of nacnac amongst synthetic chemists is driven, in part, by the monoanionic nature of the β-diketiminate group, the chelating nature but also variable mode of hapticity, the ease in preparation, and the versatility to tune both electronic and steric parameters.[1] Therefore, it is of no surprise that nacnac ligands can stabilize most elements of the periodic table to form main-group, transition-metal, lanthanide, and actinide complexes.[1]



Scheme 1. General representation of cyclopentadienyl and nacnac ligands.

The first documented cases of β-diketiminate metal complexes were reported by McGeachin[2] and Parks and Holm[3] in 1968. In their studies, the metal of choice was Ni^{II}, as two N-substituted β-diketiminate ligands could be used to sterically tune the Ni^{II} ion through a range of geometries from square-planar to tetrahedral. Now, more than 40 years later, Limberg and co-workers demonstrate that a sterically modified version of the β-diketiminate ligand used in 1968 can also stabilize unsaturated $\{(\{ArNC(tBu)\}_2CH)Ni^I\}$ (Ar = 2,6-$iPr_2C_6H_3$) scaffolds, and by tweaking the conditions to generate the Ni^I complex, these systems can be made to activate and reduce the bond order of a chemically resistant and biologically relevant molecule such as N_2. In their studies, Limberg and co-workers use several synthetic approaches to isolate and characterize the complexes $[\{(\{ArNC(tBu)\}_2CH)Ni\}_2(\mu_2,\eta^1:\eta^1\text{-}N_2)]^{x-}$ ($x = 0, 1, 2$), therefore allowing them to collect one-electron reduction snapshots of two nickel centers bridged by N_2.[4] An outline of these synthetic strategies is described in Scheme 2. Impressively, Limberg and co-workers are able to isolate a neutral complex (**4**) and odd or evenly charged (complexes **5** and **6**) reduction products stemming from a precursor material (**1**). The authors perform a series of spectroscopic studies to elucidate the connectivity and spin state of these paramagnetic complexes, including single-crystal X-ray diffraction studies and theoretical analysis of their frontier orbitals. In their studies, it was independently found that the monoanion N_2 salt **5** could be prepared by comproportionation reactions using the appropriate stoichiometry of **1** and **6** or **4** and **6** (Scheme 2).

Surprisingly, few N_2 complexes of nickel are known,[5] therefore making the present work[4] a gigantic leap towards N_2 activation and reduction using a 3d late transition metal such as nickel. Holland and co-workers reported a similar group of complexes featuring iron as the central metal.[6] In those studies, treatment of $[(\{ArNC(tBu)\}_2CH)FeCl]$ with a strong reductant such as $NaC_{10}H_8$ resulted in N_2 activation to afford the neutral species $[\{(\{ArNC(tBu)\}_2CH)Fe\}_2(\mu_2,\eta^1:\eta^1\text{-}N_2)]$. Addition of two equivalents of strong reductant (K or Na metal) engendered formation of the dianionic salt, analogous to the nickel complex **6** shown in Scheme 2.[6] Table 1 summarizes the vibrational frequencies and metrical parameters for the N–N motif for both neutral and charged metal species. For comparison, the vibrational frequency and N–N bond length of free N_2 has been also included. From the data, it can be assessed that reduction in the bond order of the activated N_2 unit is more pronounced in the iron system than in the nickel system. The data also reconciles the fact that **4** exchanges more rapidly with free N_2 than the neutral Fe analogue.[4,6] The structures for $K_2[\{(\{ArNC(tBu)\}_2CH)M\}_2(\mu_2,\eta^1:\eta^1\text{-}N_2)]$ (M = Fe, Ni) are also analogous regarding the linearity of the MN_2M bridge and placement of

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[*] Prof. Dr. D. J. Mindiola
Department of Chemistry, Indiana University
Bloomington, IN 47405 (USA)
Fax: (+1) 812-855-8300
E-mail: mindiola@indiana.edu

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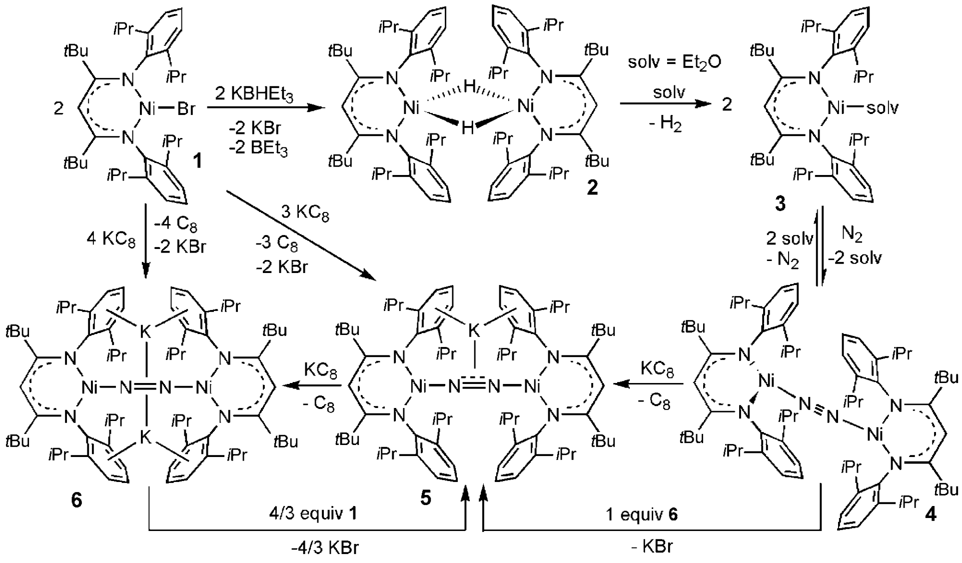


Scheme 2. Synthetic approach to preparing dinuclear nickel complexes with an activated N$_2$ ligand.

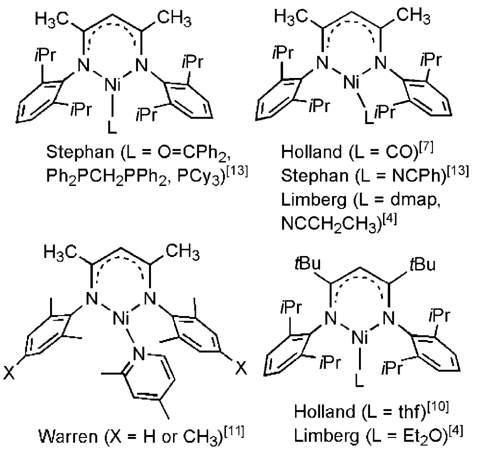
Table 1: Reported stretching frequencies (cm^{-1}) and bond lengths (Å) for the N–N bond of free N$_2$ and activated forms.[a]

	N$_2$	[{Fe}$_2$N$_2$]	[{Fe}$_2$N$_2$]$^{2-}$	4	5	6
$\tilde{\nu}_{\mathrm{IR}}$	–	–	–	2164	–	–
$\tilde{\nu}_{\mathrm{Raman}}$	2331	1778	1589	–	1825	1696
d(NN)	1.098	1.182(5)	1.241(7)	1.120(4)	1.143(8)	1.185(8)

[a] {Fe} represents the scaffold {([ArNC(*t*Bu)]$_2$CH)Fe} (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$).

the K$^+$ ion. These compounds are not discrete salts, since the K$^+$ ions interact with the N$_2$ unit and the aryl moieties of the β-diketiminate ligand. In fact, the molecular structure of **5** shows a topologically linear NiN$_2$Ni bridge, arguably suggesting that the K$^+$ ions enforce this type of geometry. On the other hand, the solid-state structures of the neutral species $[\{(\{\mathrm{ArNC}(t\mathrm{Bu})\}_2\mathrm{CH})\mathrm{M}\}_2(\mu_2,\eta^1{:}\eta^1\text{-}\mathrm{N}_2)]$ differ substantially between the nickel and iron systems. In the case of M = Ni, the geometry about each $\{(\{\mathrm{ArNC}(t\mathrm{Bu})\}_2\mathrm{CH})\mathrm{Ni{-}N}\}$ sphere is T-shaped, with the aryl groups oriented almost orthogonal to each other to avoid steric clashing. For M = Fe, there is no such distortion, allowing for formation of a system having approximate D_{2h}/D_{2d} symmetry. However, Holland and co-workers crystallized both a linear form and a distorted form analogous to **4** when the β-diketiminate ligand was reduced in size to $\{\mathrm{ArNC}(\mathrm{CH}_3)\}_2\mathrm{CH}^-$.[6] Do packing forces or electronics dominate the geometrical features observed in these systems? Y- to T-shaped distortion geometries for three-coordinate systems of the type $[(\{\mathrm{ArNC}(t\mathrm{Bu})\}_2\mathrm{CH})\mathrm{M{-}X}]$ have been explored for d^4 and d^9 3d transition-metal complexes. In both cases, the distortion has been assessed to be electronic in nature, with sterics playing only a secondary role. Specifically, distortion has been ascribed to both differential charge donation and Pauli repulsions of the third donor X.[7,8]

Prior to β-diketiminates ligands taking the spotlight in stabilizing unusually low-coordination environments of mononuclear Ni$^{\mathrm{I}}$, examples of such systems were scant.[9] As a result, the pursuit of Ni$^{\mathrm{I}}$ complexes stabilized by a β-diketiminate ligand represents an active area of research that was initially triggered by the Holland group with the report of the compounds $[(\{\mathrm{ArNC}(t\mathrm{Bu})\}_2\mathrm{CH})\mathrm{Ni(thf)}]$[10] (Y-shape) and subsequently $[(\{\mathrm{ArNC}(\mathrm{CH}_3)\}_2\mathrm{CH})\mathrm{Ni(CO)}]$ (T-shape; Scheme 3).[7] The groups of Warren and Stephan complemented the series by preparing the Ni$^{\mathrm{I}}$ complexes $[(\{\mathrm{Ar'NC}(\mathrm{CH}_3)\}_2\mathrm{CH})\mathrm{Ni}(2{,}4\text{-lutidine})]$ (Ar′ = 2,6-Me$_2$C$_6$H$_3$),[11] and the dinuclear species $[\{(\{\mathrm{ArNC}(\mathrm{CH}_3)\}_2\mathrm{CH})\mathrm{Ni}\}_2(\mu\text{-}\eta^3{:}\eta^3\text{-}\mathrm{C}_6\mathrm{H}_5\mathrm{Me})]$,[12] respectively (Scheme 3). Stephan elegantly demonstrated that the toluene ligand of the latter species can be replaced with a plethora of substrates such as alkynes, olefins, benzophenone, nitriles, and phosphines.[13] By slightly modifying reaction conditions and the steric nature of the β-diketiminate ligand, Limberg and co-workers have optimized a Ni$^{\mathrm{I}}$ system that can activate N$_2$



Scheme 3. Reported β-diketiminate complexes featuring mononuclear, three-coordinate Ni$^{\mathrm{I}}$ centers. Cy = cyclohexyl, dmap = dimethylaminopyridine

apart from the more common donor ligands. Consequently, examples of three-coordinate Ni^I β-diketiminate complexes are now becoming more and more numerous (Scheme 3).

Despite the availability Fe or Ni species of the type $[\{(\{ArNC(tBu)\}_2CH)M\}_2(\mu_2,\eta^1:\eta^1\text{-}N_2)]^{x-}$ ($x = 0$, 1, and 2), the N_2 unit in question is not susceptible to functionalization, presumably owing to the ability of the metal to readily eject an electron concurrent with N_2 liberation. Hence, these compounds are best regarded as electron reservoirs, whereby the MN_2M π^* orbitals behave as a storage unit, an attribute arising from the N_2 ligand itself. Although there are some limitations to these N_2-bridged systems, the β-diketiminate ligand will still continue to draw attention, especially given how sensitive the metal in question can be to reaction conditions and degree of steric congestion offered by this ancillary support. The Limberg group's work is another testimony to how small variables can yield unprecedented outcomes. We are left wondering why their chemistry resulted in N_2 activation, unlike work by the groups of Holland, Stephan, and Warren. Could this be because of different preparatory conditions for the Ni^I system, such as the absence of coordinating solvents? You can never learn too much from one system. As a result, nacnac ligands are still prevalent in coordination chemistry, despite their many different modes of decomposition.[1] Nacnac, vos es etiam illic! (You are still there!).

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